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TWO FIBROUS IRON SULFIDES AND VALLERIITE FROM CYPRUS WITH NEW DATA ON VALLERIITE[1]

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ABSTRACT

Two fibrous iron sulfide minerals, with optical and physical properties similar to valleriite, are described from an ultrabasic complex located near Pefkos, Cyprus. The two minerals, designated in this paper as Type I and Type II, occur as fine-grained aggregates and/or veinlets of fibrous crystals surrounding troilite.

Electron microprobe analyses of the Type I phase suggest a formula $2FeS \cdot 0.84 (CaCO_3 \cdot H_2O)$. The mineral readily effervesces in dilute hydrochloric acid releasing an odour of H_2S. Infrared and DTA studies show the presence of bonded H_2O. The powder pattern, indexed on a hexagonal cell, gave dimensions $a = 3.83$, $c = 33.12$ Å.

Electron microprobe analyses of the Type II phase suggest a formula $2FeS \cdot 1.58(Mg_{0.53}Fe_{0.47}(OH)_2)$. The mineral does not effervesce in hydrochloric acid. The powder pattern resembles but is distinct from that of valleriite and of the Type I phase and can be indexed on a hexagonal cell with $a = 3.74$, $c = 32.63$ Å. The mineral has also been identified in a specimen of troilite from the "del Norté Co." locality in California. This phase appears to be similar to the "fibrous iron sulfide," previously described from the Muskox Intrusion, N.W.T. and from the Lizard ultramafics in Cornwall, England.

Where sufficient material was available, infrared and Mössbauer spectra of the two phases have been examined and compared to those of normal valleriite from Sweden. As they are clearly members of a group of minerals which includes valleriite, the problem of their nomenclature and classification is also discussed.

INTRODUCTION

A preliminary mineralogical study of samples from the ultrabasic complex of Pefkos, in the southern part of the island of Cyprus, was undertaken by Prof. A. P. Millman of University College, Cardiff. Bulk chemical analysis showed the presence of major iron and sulfur and minor calcite, copper, nickel, arsenic, cobalt, and insoluble fraction. A study of polished sections of this material showed major "pyrrhotite" with exsolved pentlandite, veined by a later complex mineral resembling valleriite. Microchemical tests confirmed the presence of iron and sulfur in this phase but not copper. Gersdorffite and calcite also occurred in the veins.

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Recently, a sample of this material obtained from Prof. Millman was examined in detail with the object of undertaking a study of the crystal chemistry of valleriite by Mössbauer spectroscopy. Electron microprobe analysis of the valleriite–type material revealed the presence of only minor amounts of true valleriite but appreciable quantities of two other fibrous iron sulfide phases. These phases have been characterised in terms of their compositions, structures and physical and optical properties. Where sufficient material was available, infrared and Mössbauer spectra of these phases have been examined and compared to those of normal valleriite from Sweden.

The object of these studies has been not only to characterise the two fibrous iron sulfides but also to explain their relationship to each other and to valleriite.

THE PEFKOS DEPOSIT

This ultrabasic complex, a property of the Hellenic Mining Company, is located near Pefkos in the southern part of the island of Cyprus, north of the port city of Limassol. An excellent account of the geology and mineralogy of this deposit and of other similar ones in the area has been given by Antun, El Goresy, and Ramdohr (1966).

From observations made on the specimen available for this study, it appears that the fibrous iron sulfide minerals formed during serpentinization of the ultrabasic rock from alteration of existing primary sulfides, in particular troilite. Antun *et al.* describe the major sulfide phase as pyrrhotite whereas troilite is clearly the major phase in the sample studied here. The troilite may be restricted in its occurrence in the deposit and may account for the unusual assemblage.

Minor amounts of valleriite are present and the amount seems to be controlled by the presence of primary copper–bearing sulfides in the rock. The primary sulfides and arsenides are troilite, chalcopyrite, maucherite, cobaltite, and pentlandite. Secondary minerals which appear to have formed from the chalcopyrite are valleriite, mackinawite, chalcocite, covellite, and euhedral magnetite. The troilite has altered to euhedral magnetite and to two fibrous iron sulfides, designated in this paper as Type I and Type II phases. Also present are "chrome–spinel", magnetite, calcite, serpentine–like minerals, and probably talc.

ELECTRON MICROPROBE ANALYSES

The mineral compositions were obtained with a Materials Analysis Company electron microprobe. In most cases, one or several of synthetic FeS, FeS_2, $FeAs_2$, MgO, pure metallic Cu, Co, or Ni were used as standards. The final compositions were derived by processing the

X–ray intensities with Rucklidge's (1967) computer program for reduction of electron microprobe data.

Type I

This phase is the most abundant of the two fibrous iron sulfide minerals and when identification is based on optical properties alone, it can easily be mistaken for valleriite. Its colour varies from a dull greyish buff to a bronze, whereas valleriite is buff with a tinge of grey. Anisotropism is extreme and varies from white to a bright reddish yellow. Valleriite by comparison is golden yellow. The mineral commonly occurs as a fine–grained aggregate surrounding troilite (Figure 1a and b) but also occurs as clusters and veinlets of fibrous crystals up to 250 microns in size (Figure 1c). The hardness of the mineral could not be measured by indentation due to its fibrous nature. However, the nature of the polished surface suggests that the hardness is close to valleriite. The reflectivity could not be measured.

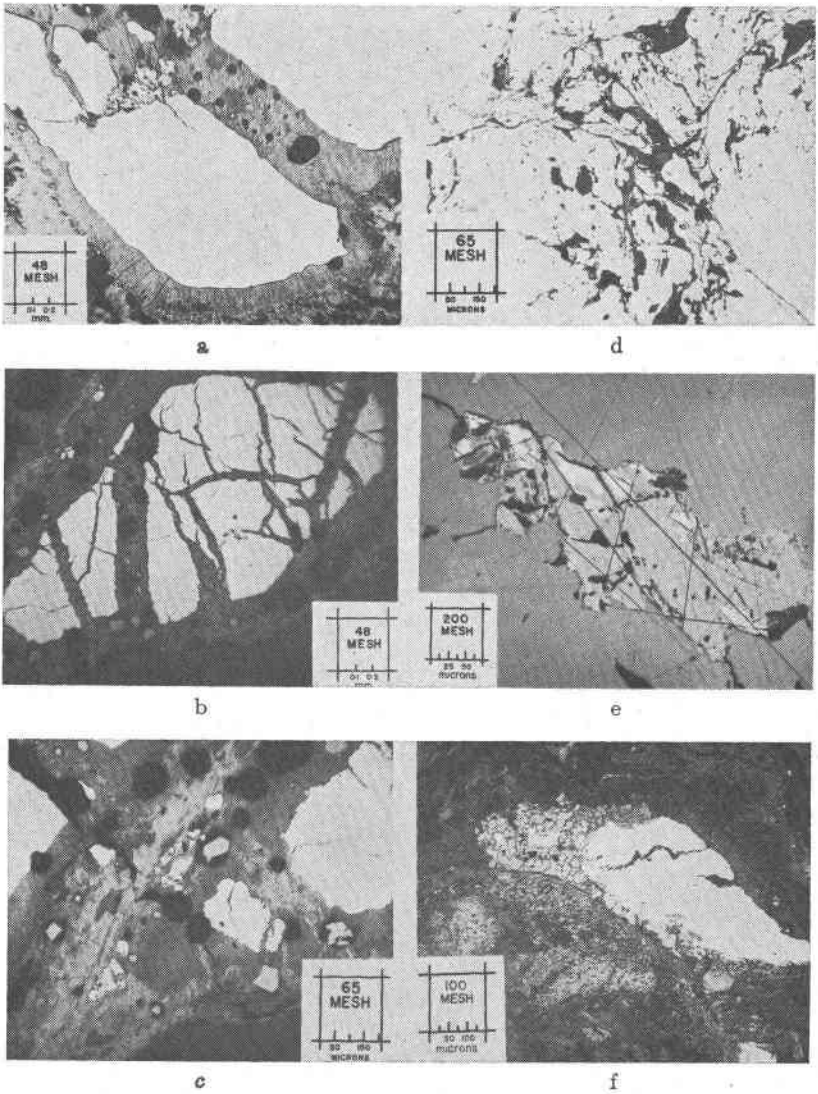
Electron microprobe analysis in four separate sections yielded the results shown in Table 1. No other elements down to atomic number 11(Na) could be detected; in particular, copper, aluminum, and magnesium were sought, but not found. The mineral does not effervesce in acetic acid but readily effervesces in dilute hydrochloric acid (1:3 solution) releasing an odor of H_2S. Infrared and differential thermal analysis studies, discussed later, show the presence of bonded OH or H_2O. The formula of the mineral is proposed as $(2FeS)\cdot 0.84(CaCO_3\cdot H_2O)$. The calculated values of CO_3 and H_2O are also given in Table 1 and combined with the microprobe analyses these give a total of 100.84 percent.

Material suitable for single crystal studies was not available but the powder pattern which resembles valleriite, although distinct, is given in Table 2. This has been indexed on a hexagonal cell with dimensions $a = 3.83 \pm 0.02$, $c = 33.12 \pm 0.02$ Å.

Type II

The optical properties of this phase are also very similar to valleriite and its identification could be confirmed only by microprobe analysis. The colour is less intense than valleriite and is greyish tinted buff. Extreme anisotropism is exhibited with colors of white–greyish–orange–yellow. The reflectivity was measured at four standard wavelengths and the values compared to those of valleriite are given in Table 3. The mineral occurs as clusters of fibrous to lath–shaped crystals and as veinlets interstitial to the troilite grains sometimes rimmed by the Type I phase. The clusters range up to 150 microns in size. The mineral is commonly associated with valleriite both as separate clusters and as interlocking laths.

Microprobe analysis in three separate sections yielded the results in Table 4. Again, no other elements down to atomic number 11 (Na) could be detected. The balance of the analyses is ascribed to (OH) yielding the average formula $2FeS \cdot 1.58(Mg_{0.53}Fe_{0.47}(OH)_2)$; combining the calculated (OH) concentration with the microprobe analyses



gives a total of 101.2 percent. The mineral does not effervesce in either acetic or hydrochloric acid.

Material suitable for single crystal studies was not available, but the powder pattern is given in Table 5. The pattern resembles, but is distinct from, valleriite and the Type I phase and it can be indexed on a hexagonal cell with $a = 3.74 \pm 0.02$, $c = 32.63 \pm 0.02$ Å. The unindexed extra reflection may be due to impurities.

Subsequent to this study, another occurrence of this mineral was noted in a specimen of troilite from the "del Norté Co." locality in California. The specimen, labelled as troilite, was obtained from the Royal Ontario Museum Collection M12906.

The phase has formed from alteration of troilite as shown in Figure 1d. The analysis is given in Table 4. The remainder of the analysis is ascribed to (OH) yielding the formula $2FeS \cdot 1.64(Fe_{.77}Mg_{.23}(OH)_2)$. An X-ray powder pattern of this mineral is identical to that from the Cyprus deposit. The main differences in the mineral from the two

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FIG. 1.—(a) Photomicrograph of troilite (white) partially replaced peripherally by the Type I phase. The Type I phase in close proximity to the troilite has a radial texture. The black rounded areas are holes, some containing euhedral magnetite.

(b) Photomicrograph of fractured troilite (white) partially replaced by the Type I phase. The small grey euhedral crystals are magnetite. The small white inclusion in the centre of the troilite grain is pentlandite.

(c) Photomicrograph of troilite remnants (white) partially replaced by the Type I phase. The grain size of this mineral increases from a dense, fine-grained mass near the troilite to bundles of fibrous crystals further out. The euhedral white crystal are magnetite while irregular grains of pentlandite occur mainly in the fibrous section of the mineral. The black areas are holes.

(d) Photomicrograph of the Type II mineral (light grey) forming along fractures in deformed troilite (white). The darker grey material with the Type II phase is gangue (del Norté Co., California).

(e) Photomicrograph (crossed nicols) of mackinawite inclusions (white) in pentlandite (light grey). The surrounding material is troilite. The greyish black inclusions are valleriites and the black areas are holes.

(f) Photomicrograph of a troilite remnant (white) with one half of the fragment altered to euhedral magnetite and what appears to be bornite. Although not readily visible, chalcopyrite occurs rimming the troilite where the grain is replaced.

TABLE 1

Microprobe Analyses of the Type I Mineral

	(1)	(2)	(3)	(4)	Average
Ca	12.44	12.70	12.14	12.57	12.46 ± 0.4
Fe	40.55	40.30	41.11	39.73	40.42 ± 0.6
S	24.02	23.89	22.61	24.30	23.71 ± 0.6
	77.01	76.89	75.86	76.60	76.59
Calc. CO_3	18.62	19.02	18.18	18.84	18.66
Calc. H_2O	5.58	5.70	5.45	5.65	5.59
	101.21	101.61	99.49	101.09	100.84

CO_3 (calculated) = Amount of CO_3 required to combine with analysed quantities of Ca to give $CaCO_3$.

H_2O (calculated) = Amount of H_2O required to give one molecule with the $CaCO_3$ fraction.

(1) $2(Fe_{.97}S_{1.00}) \cdot 0.83(CaCO_3 . H_2O)$

(2) $2(Fe_{.97}S_{1.00}) \cdot 0.85(CaCO_3 . H_2O)$

(3) $2(Fe_{1.04}S_{1.00}) \cdot 0.86(CaCO_3 . H_2O)$

(4) $2(Fe_{.94}S_{1.00}) \cdot 0.83(CaCO_3 . H_2O)$

occurrences is the higher iron content of the hydroxide layer in the "del Norté" sample. Other minerals identified in the polished section are sphalerite, pentlandite, chromite, and minor amounts of valleriite. The valleriite occurs either as distinct veinlets or as interlocking laths with the Type II phase. Microprobe analysis of the valleriite gave a formula of $(Cu_{.65}Fe_{1.35}S_{2.00})\cdot 1.49(Mg_{0.68}Fe_{0.18}Al_{0.16}(OH)_2)$.

The Type II mineral appears to be similar to the "fibrous iron sulfide" described by Jambor (1969) in the Muskox Intrusion, N.W.T. and by Clark (1970) from the Lizard ultramafics in Cornwall, England.

Associated Minerals

Troilite is the major mineral constituent in the sample. The most characteristic feature of the mineral is its intense fracturing and alteration to the fibrous iron sulfide minerals (Figure 1a, b, c). The mineral was originally identified by its composition and confirmed by X-ray powder diffraction using a Guinier camera. Electron microprobe analyses and etch tests using a solution of HI show that the phase is homogeneous. Three separate determinations gave Fe 63.94, 63.92, 63.89; S 36.38, 35.42, 36.90; totals 100.32, 99.34, 100.79 wt. percent respectively. The

TABLE 2

X-Ray Powder Diffraction Data of the Type I Mineral from Pefkos, Cyprus; 114.6-mm-diameter camera, Fe-filtered Co radiation
a = 3.83 ± 0.02Å c = 33.12 ± 0.02Å

hkℓ	d(calc.)Å	d(meas.)Å	I(est)
00.3	11.040	10.98	10
00.6	5.520	5.52	10
----	------	3.83	1
00.9	3.680	3.66	7
10.1	3.300	3.30	3
10.4	3.079	3.05	3
10.6	2.843	2.84	8
00.12	2.760	2.72	2
$10.\overline{8}$	2.589	2.58	2
10.9	2.464	2.46	4
$10.\overline{11}$	2.229	2.24	6
00.15	2.208		
----	------	2.16	1/2
----	------	2.07	3
10.13	2.020	2.00	1
$10.\overline{14}$	1.926	1.942	1
11.3	1.887	1.879	1/2
00.18	1.840	1.851	6
11.6	1.809	1.825	2
11.7	1.775	1.785	1
10.16	1.756	1.749	4
00.21	1.577	1.584	1
$20.\overline{16}$	1.294	1.298	2

TABLE 3

Reflectivity of the Type II Mineral and Valleriite from Cyprus

		470nm	546nm	589nm	650nm
Valleriite	max.	14.8	17.6	18.8	20.6
	min.	12.0	11.6	11.7	12.3
Type II Mineral	max.	12.2	14.1	15.7	18.5
	min.	11.2	10.7	10.8	11.0

The reflectance measurements were made on a Leitz MPV reflectance apparatus equipped with an MPE photometer, and were made against carborundum standard no. 2538.26, provided by the Commission on Ore Microscopy and calibrated by the N.P.L. A 60:1 objective with a numerical aperture of 0.95 was used.

TABLE 4

Microprobe Analyses of the Type II Mineral

	Cyprus			Average	Del Norté Co. Calif.
	(1)	(2)	(3)		
Mg	6.78	6.76	6.79	6.78 ± 0.2	2.86
Fe	50.99	50.63	51.00	50.87 ± 0.2	56.53
S	21.60	21.62	21.33	21.52 ± 0.6	19.92
	79.37	79.01	79.12	79.17	79.31
Calc. (OH)	21.25	21.84	23.01	22.03	23.95
	100.62	100.85	102.13	101.20	103.26

OH calculated = Amount of OH required to combine with analyzed quantities of Mg and the Fe in excess of that to give FeS. OH with Fe, calculated as $Fe(OH)_3$.

(1) $2FeS \cdot 1.54(Mg_{.54}Fe_{.46}(OH)_2)$

(2) $2FeS \cdot 1.51(Mg_{.54}Fe_{.46}(OH)_2)$

(3) $2FeS \cdot 1.68(Mg_{.50}Fe_{.50}(OH)_2)$

Del Norté Co. $2FeS \cdot 1.64(Fe_{.77}Mg_{.23}(OH)_2)$

average of the analyses gives a formula $Fe_{1.01}S_{1.00}$. Ni; Co and Cu were not detected.

Pentlandite is a minor constituent and occurs as irregular grains, either within the troilite or in the Type I mineral. The pentlandite appears very resistant to alteration and the fibrous iron sulfide minerals have not formed from it. While most of the grains are homogeneous, others contain small inclusions of mackinawite (Figure 1c). It was first thought that the mackinawite has formed from the pentlandite, but closer examination revealed that the host mineral is a pale yellow phase. Electron microprobe analyses of the pentlandite gave: Co 6.3, Ni 23.6, Fe 38.0, S 32.4; total 100.3 wt. percent, corresponding to the formula $(Co_{0.8}Ni_{3.2}Fe_{5.4})_{9.4}S_{8.0}$. Microprobe analyses of the mackinawite gave Co 1.8, Ni 2.1, Fe 60.3, S 36.2; total 100.4 wt. percent, corresponding to the formula $(Co_{0.03}Ni_{0.03}Fe_{0.96})_{1.02}S_{1.00}$.

Chalcocite, covellite, chalcopyrite, and bornite are present in the ore, although in very minor amounts. Covellite was found only as a veinlet, while chalcocite occurs as irregular grains usually in the vicinity of valleriite. Chalcopyrite is very rare and occurs rimming or along cracks in the troilite remnants which it appears to be replacing. The identification of bornite is questionable, and what has been termed bornite forms the matrix of a cluster of magnetite crystals which have formed from the alteration of troilite (Figure 1f).

Cobaltite and maucherite occur either as separate grains or as composite grains associated with the troilite. Maucherite can be distinguished from cobaltite by its weak anisotropism and a pinkish cast. The identities of the two minerals were confirmed by X–ray powder diffraction and electron microprobe analyses. The analysis of cobaltite gave Fe 3.31, Ni 8.29, Co 23.75, As 48.47, S 17.02; total 100.83 wt. percent giving a formula of $(Fe_{0.10}Ni_{0.23}Co_{0.61})_{1.00}As_{1.07}S_{0.88}$. Analysis of maucherite gave Co 3.06, Fe 1.10, Ni 47.48, As 47.53; total 99.49 wt. percent corresponding to the formula $(Fe_{0.22}Co_{0.68}Ni_{10.36})_{11.3}As_{8.0}$. "Chrome spinel" is widespread and occurs as irregular porous grains, usually intergrown with or rimmed by magnetite. It appears that the idiomorphic spinel and magnetite are the primary minerals.

Infrared and Mössbauer Spectra

Infrared spectra were obtained of the Type I mineral and of valleriite from Kaveltorp (ROM 17023) using a Beckman IR–12 instrument with cesium iodide as the matrix material. Spectra were recorded over the range 200–4,000 cm^{-1} and for both materials features at 1,620 cm^{-1} and 3,600 cm^{-1} may be assigned to bonded water or (OH) radi-

TABLE 5

X-Ray Powder Diffraction Data of the Type II Mineral from Pefkos, Cyprus; 114.6-mm-diameter camera, Fe-filtered Co radiation a = 3.74 ± 0.02Å c = 32.63 ± 0.02Å R$\bar{3}$m

hkℓ	d(calc.)Å	d(meas.)Å	I(est)
00.3	10.876	10.86	8
00.6	5.438	5.42	10
00.9	3.625	3.606	2
10.1	3.224	3.222	1/2
00.12	2.719	2.713	3
----	-----	2.602	4*
10.$\bar{8}$	2.537	2.535	1/2
10.10	2.299	2.301	4
----	-----	2.233	3*
00.15	2.175	2.183	2
----	-----	2.125	2*
11.0	1.870	1.876	1/2
11.3	1.843	1.838	5
00.18	1.813	1.804	3
11.6	1.769	1.765	1/2
00.21	1.554	1.571	2
00.24	1.359	1.351	2

*extra reflections that cannot be indexed using the structure of Evans and Allmann (1968). These may represent unidentified impurities.

cals. Weak features in the region 1,450 cm^{-1} may be due to CO_3 groups but are unfortunately inconclusive. The spectra are shown in Figure 2.

The Mössbauer spectra of the Kaveltorp valleriite and a sample containing Type I and minor amounts of the Type II minerals from Cyprus were determined using an Austin Science Associates drive unit with a Co^{57} source in Cu and a Northern Scientific multichannel analyser. Spectra obtained at 300°K and 77°K were interpreted using a least squares fit computer programme and the spectrometer was calibrated with iron foil. The spectra are shown in Figure 3 and at this stage only tentative interpretations may be offered for these complex spectra. The spectrum of normal valleriite at 300°K resembles spectra obtained for high–spin Fe^{3+} exhibiting magnetic relaxation. The spreading out of the spectrum at 77°K is in agreement with this interpretation. This suggests a formal valence scheme of the type $Cu^{+}Fe^{3+}S_2$ for the sulphide layer.

The complex spectrum derived from the Cyprus sample again suggests magnetic relaxation, substantiated by the spreading of the spectrum at 77°K. At this temperature it is possible to distinguish the outer peaks of a hyperfine magnetic subspectrum with an internal field at 254 Kgauss. This value and the isomer shift (0.67 mm/sec) show rea-

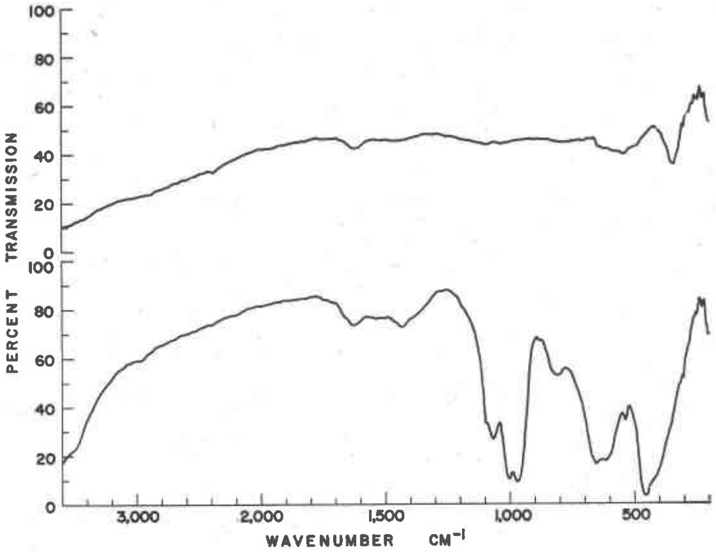

FIG. 2.—Infra-red absorption spectra of valleriite from Kaveltorp, Sweden (lower curve) and the Type I mineral from Cyprus (upper curve).

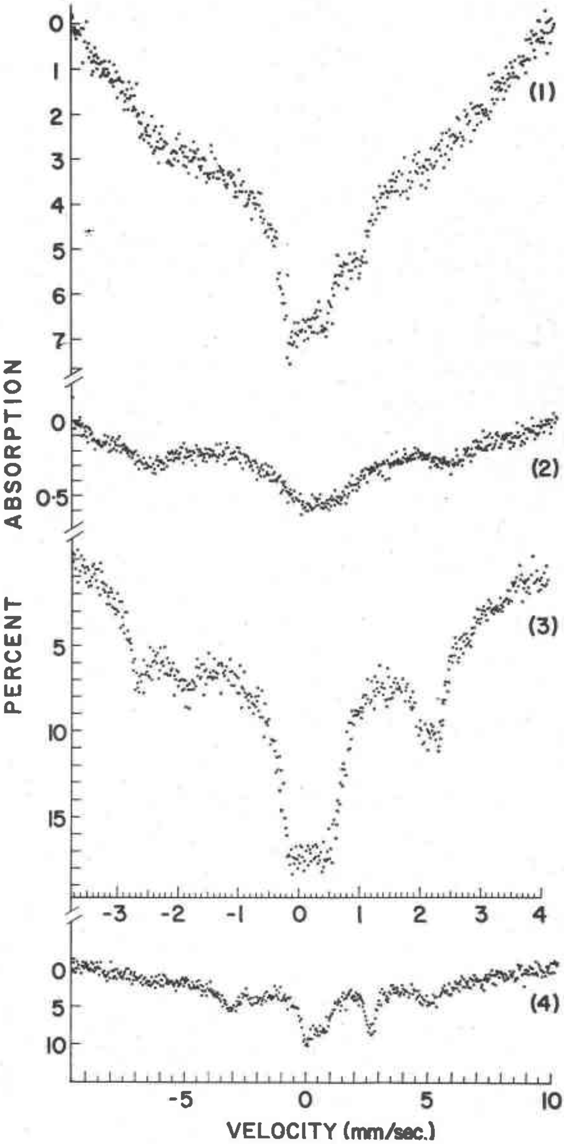

FIG. 3.—Mössbauer spectra of valleriite from Kaveltorp at 300°K (Spectrum 1) and 77°K (Spectrum 2) and of the Type I (with some Type II) mineral at 300°K (Spectrum 3) and 77°K (Spectrum 4).

sonable agreement with reported values for high-spin Fe^{2+} in sulphides although further changes may take place at lower temperatures.

DIFFERENTIAL THERMAL ANALYSIS

Samples of Kaveltorp valleriite and the Type I (with some Type II) phase from Cyprus were also examined by differential thermal analysis. The analyses were carried out under the same conditions for both samples, that is on a platinum foil disc in a vertical furnace in an atmosphere of flowing argon. The traces are shown in Figure 4. The first peak occurs at 114°C for valleriite and 135°C for Type I and Type II material. These peaks are interpreted as the initial breakdown temperatures of the phases due to the loss of (OH) or H_2O from the structure. Reaction continues over the range 114–158°C for valleriite and 135–197°C for Types I and II. The other major feature in the valleriite trace is on endothermic peak at 590°C. Types I and II do not exhibit this feature but a sharp endothermic peak at 896°C corresponds to the decomposition temperature of $CaCO_3$.

An upper stability temperature between 600°C and 650°C was suggested for the valleriites synthesised by Iiishi, Tomisaka, Kato, and Takeno (1970), the compositions of which were in the range of 2.0 $(Mg_{0.68}Al_{0.32}(OH)_2)\cdot CuFeS_2$ to $2.3(Mg_{0.68}Al_{0.32}(OH)_2)\cdot CuFeS_2$.

THE CRYSTAL CHEMISTRY AND CLASSIFICATION OF VALLERIITE–TYPE MINERALS

When Evans and Allmann (1968) demonstrated that valleriite belongs to a group of minerals that are "hybrid" structures, consisting of alternating brucite–like and copper–iron–sulfide layers, they suggested the possibility of further substitution in at least the brucite–type layer. That further substitutions do occur in this layer was shown by the work of Springer (1968) and of Harris, Cabri, and Stewart (1970). The present work on the Cyprus and del Norté Co. materials, together with observations made by Jambor (1969) and Clark (1970), also show that copper is not always present in the sulfide layer. A list of compositions for "valleriite–type" minerals are given in Table 6.

The Type II phase from Cyprus and the virtually identical phases from California and USSR are probably the same phase as that described by Jambor and by Clark. The existence of this phase clearly shows that the sulfide layer in "valleriite–type" minerals is of two distinct types: an FeS (or $Fe_{1-x}S$) layer and a (Cu,Fe)S layer in which the ratio of Cu:Fe is close to 1:1. There is no clear evidence to suggest that the Cu:Fe ratio deviates from 1:1 and the variation shown in Table 6 may be due to analytical error. If substitution in the sulfide

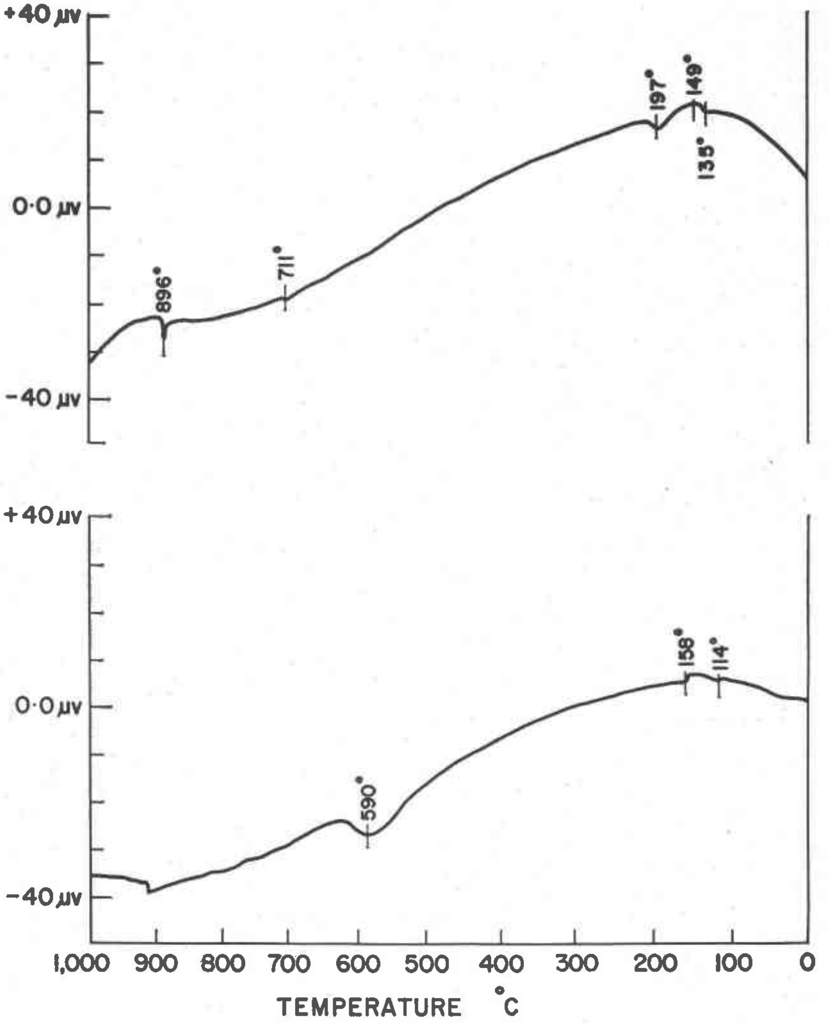

Fig. 4.—Differential thermal analysis curves of valleriite from Kaveltorp (lower curve) and the Type I (with some Type II) phase from Cyprus (upper curve).

layer were possible, then one would expect to find intermediate compositions in samples containing both normal valleriite and the Type II material. This is not the case in the samples from either Cyprus or California where both minerals occur together. In fact, the rather low copper content for the del Norté Co. valleriite may be due to admixtures of the Type II phase which could not be distinguished optically.

TABLE 6

Chemical Compositions of "Valleriite-Type" Minerals

Locality	Formula
Kaveltorp, Sweden (Type locality)	$(Cu_{.81}Fe_{1.19}S_2) \cdot 1.56(Mg_{.83}Fe_{.17}(OH)_2)$ (Springer, 1968)
Kaveltorp, Sweden	$(Cu_{.87}Fe_{1.13}S_2) \cdot 1.44(Mg_{.79}Fe_{.21}(OH)_2)$ (Harris, unpublished analysis)
Loolekop, Palabora South Africa	$(Cu_{.95}Fe_{1.05}S_2) \cdot 1.57(Mg_{.73}Al_{.27}(OH)_2)$ (Springer, 1968)
Loolekop, Palabora South Africa	$(Cu_{1.04}Fe_{.96}S_2 \cdot 1.67(Mg_{.75}Fe_{.16}Al_{.09}(OH)_2)$ (Springer, 1968)
New Imperial Mine, Yukon, Canada	$(Cu_{1.19}Fe_{.81}S_2) \cdot 1.64(Mg_{.71}Al_{.23}Fe_{.06}(OH)_2)$ (Petruk <u>et al,</u> 1970)
Noril'sk, Western Siberia	$(Cu_{1.00}Fe_{1.00}S_2) \cdot 1.47(Fe(OH)_2)$ (Harris <u>et al,</u> 1970)
Del Norté Co. California	$(Cu_{.65}Fe_{1.35}S_2) \cdot 1.49(Mg_{.68}Fe_{.18}Al_{.16}(OH)_2)$ (This study)
Muskox, N. W. T. Canada	$3FeS \cdot 2(Mg,Fe)(OH)_{2+n}$ (Jambor, 1969)
Cyprus, Type II	$2FeS \cdot 1.58(Mg_{.53}Fe_{.47}(OH)_2)$ (This study)
Del Norté Co. California	$2FeS \cdot 1.64(Fe_{.77}Mg_{.23}(OH)_2)$ (This study)
Voronezh region* USSR	$2FeS \cdot 1.85(Mg_{.58}Fe_{.26}Al_{.16}(OH)_2)$ (Harris, unpublished)
Cyprus, Type I	$2FeS \cdot 0.84(CaCO_3 \cdot H_2O)$ (This study)

*This mineral has been named tochilinite of monoclinic symmetry. Organova <u>et al</u>. (1971).

Admixtures of the Type II phase may also account for the low copper values in the Kaveltorp valleriite.

The Type I mineral, although a "valleriite–type", appears to be distinctly different with the brucite–like layer represented by a carbonate instead of a hydroxide.

The Mössbauer data obtained in this study are clearly of a preliminary nature and present considerable problems of interpretation. However, a number of interesting points do emerge. The indications of magnetic ordering in valleriite contrast with the diamagnetic or Pauli paramagnetic behaviour exhibited by iron in the structurally related mineral mackinawite (Vaughan and Ridout, 1971). However, the closest metal–metal distance in mackinawite is only 2.60 Å whereas that in valleriite is 2.77 Å. Normal valleriite probably contains ferric iron in both sulfide and oxide layers, whereas the Type I phase may contain appreciable amounts of ferrous iron. The uncertainties regarding the structures of the new phases and of valleriite itself, the problems of small and often impure samples, and the need for data obtained at lower temperatures make these conclusions tentative and call for further work on these materials.

The problem of a system of nomenclature for this group of minerals could be solved by using a scheme similar to that suggested by Levinson (1966) for the rare–earth minerals. The name "valleriite" would represent a hybrid structure mineral containing a copper–iron–sulfide and a hydroxide layer with various substitutions (Mg,Al,Fe, *etc.*) possible in the latter. The chemical symbol of the predominant element or elements in the hydroxide layer could be appended to the name valleriite, *e.g.*, the Noril'sk mineral might then be referred to as valleriite–(Fe), the Kaveltorp mineral as valleriite–(Mg,Fe) and the Palabora mineral as valleriite–(Mg,Al). The Type II phase would require a new species name with the same nomenclatural system applying to the hydroxide layer. After sufficient data are available to properly classify this mineral, the Type I phase will also require a new name.

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